EFFECTS OF THE WORKING CONDITIONS
ON THE VALUES OF THE KINETIC PARAMETERS
OF THE THERMAL DECOMPOSITIONS
OF SOME COMPLEXES

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The kinetic parameters n, A and E (the order of the decomposition reaction, the pre-exponential factor and the activation energy of the thermal decompositions) of some complexes of general formula $[MCl_2(GTD)_2]Cl$, where GTD = Girard T-diacetylmonoxime cation and M = central metal ion = Mn(II), Fe(III) and Co(II), were calculated through their TG curves. The effects of working conditions such as the sample weight and the rate of heating on the evaluated kinetic parameters are discussed.

In spite of the large number of studies reported on the thermal analysis of complexes and the calculation of their kinetic parameters [1–6], there are relatively few reports only on the effects of the conditions of the thermal decomposition processes on the values of the calculated kinetic parameters [7]. The aim of this work is to discuss the influence of changes of the sample weight and the rate of heating on the evaluated kinetic parameters of some complexes.

Experimental

The studied complexes were synthesized as mentioned in our previous paper [8], and their stoichiometry was confirmed via elemental analysis (see Table 1), UV, IR and electrical conductance.

This study was carried out with a standard derivatograph Thermoanalyzer TG–DTG–DTA (1600 °C) GDTA 16, Seteram Lyon–France. The specimens were placed in a standard platinum crucible of the instrument, fitted with a Pt–Rh thermocouple. The sample weight taken varied from 25 to 100 mg, while the rate of heating was 5, 10 or 15 deg/min.

Results and discussion

In order to characterize the TG curves obtained, the kinetic parameters n, A and E of the thermal decomposition processes were derived. Two methods were used: the Coats–Redfern [9] and Chatterjee [10] methods. they proposed two mathematical approaches for calculation of these parameters.

a) In the Coats–Redfern method, a series of relationships $-\log\left[\dfrac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] vs. \dfrac{1}{T} \times 10^3$, where α is the rate of thermal decomposition of the sample and T is the absolute temperature, were plotted for a number of assumed values of n. The correct value of n for the given thermal decomposition process yields a straight line. The value of E is calculated from the relation $E = 2.303\,R \cdot S$, where R and S are the gas constant and the slope of the obtained straight line, respectively.

b) On the other hand, the Chatterjee method is based on the general equation for the rate of a heterogeneous reaction, $v = -\dfrac{dm}{dt} = k,\, m^n$, where k, m and t are, respectively, the rate constant of the reaction, the active weight of the reacting substance, and the time elapsed from the start of the experiment. If $\log v$ is plotted against $\log m$, a straight line is obtained. Its slope is equal to n and the intercept gives $\log k$. Substituting k from the Arrhenius equation into the last equition gives:

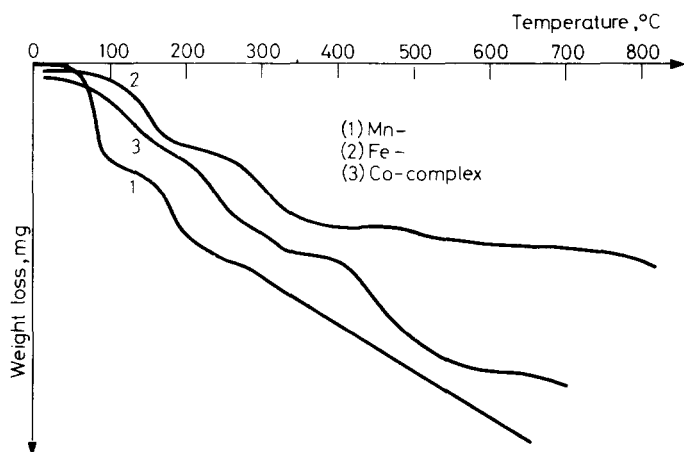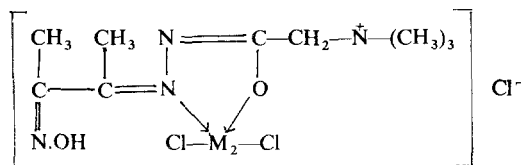$$\log v = \log A + n \log m - \frac{E}{2.303\,RT}$$

Fig. 1 TG curves for the thermal decomposition of the complexes. Sample size: 25 mg, heating rate: 5 deg/min

Table 1 Results of elemental analysis of the complexes

Complex*	C, %		H, %		N, %		M, %	
	found	(calcd.)	found	(calcd.)	found	(calcd.)	found	(calcd.)
[MnCl$_2$(GTD)$_2$]Cl	23.9	(23.6)	5.6	(5.40)	12.1	(12.27)	—	—
[FeCl$_3$(GTD)$_2$]Cl	23.3	(23.12)	5.2	(5.9)	11.9	(11.98)	—	—
[CoCl$_2$(GTD)$_2$]Cl	32.7	(32.39)	6.5	(6.28)	—	—	8.9	(8.83)

* The general structure of the studied complexes can be represented as follows [8]:

$$\left[\begin{array}{l} CH_3 \quad CH_3 \quad N =\!=\!=\!= C\!-\!CH_2\!-\!\overset{+}{N}\!-\!(CH_3)_3 \\ | | | \\ C\!-\!-\!-\!C\!=\!N O \\ \| \diagdown\!\!\diagdown \\ N.OH Cl\!-\!M_2\!-\!Cl \end{array}\right] Cl^-$$

A plot of $(\log v - n \log m)$ *vs.* $\dfrac{1}{T}$ gives a straight line, with slope $-E/2.303R$ and intercept $\log A$. TG curves of the studied complexes under one set of experimental conditions are given in Fig. 1. An analysis of the DTA curves of the complexes is shown in Table 2.

Table 2 Analysis of DTA curves of the complexes*

Complex	DTA peaks	
	endothermic	exothermic
Mc complex	Small sharp peak at 218.6 °C Broad peak at 294.2–340 °C Sharp peak at 386.4 °C	Sharp peak at 232.0 °C Small peak at 423.5 °C
Fe complex	Small sharp peak at 233.2 °C Broad peak at 268.4–810.6 °C Sharp peak at 417.8 °C	Shoulder at 246.8 °C Small peak at 487.4 °C
Co complex	Small peak at 248.1 °C Broad peak at 329.6–407.8 °C Small peak at 572.7 °C	Small peak at 268.8 °C Small peak at 527.9 °C

* Sample weight taken 50 mg, and heating rate 10 deg/min.

Kinetic parameters derived by means of both methods are presented in Table 3. It may be seen from this Table that the two methods give nearly the same values for all kinetic parameters for every complex under identical conditions.

Table 3 Kinetic parameters of thermal decompositions of the compounds studied by two different methods (rate of heating 5 deg/min, sample wt. 25 mg)

Complex	Coats–Redfern		Chatterjee method		Log A
	n	E, kcal/mol	n	E, kcal/mol	
Mn(II) complex	1.00	46.40	0.83	47.20	14.83
Fe(III) complex	1.00	50.58	0.90	51.75	13.37
Co(II) complex	1.00	55.80	1.05	56.15	12.43

The order of the decomposition reaction for all complexes is nearly unity. This means that the mechanism of the decomposition process is the same for all compounds. The E values of the complexes increase in the following sequence: Mn(II) < Fe(III) < Co(II) complex. This difference in activation energy corresponds to the difference in the nature of the central metal ion-ligand bonds, which depends mainly on the covalent character of the bonds between the metal ion and the hetero atoms of the ligand.

The covalent character and the stability of these bonds increase in the same direction.

In order to obtain a clear picture about the influences of heating rate and the sample weight on the values of the evaluated kinetic parameters, a statistical analysis of the data obtained was performed. For this purpose, the mean values of the kinetic parameters, a statistical analysis of the data obtained was performed. For this purpose, the mean values of the kinetic parameter were calculated

Table 4 Effects of changes of heating rate and sample weight on values of kinetic parameters

Rate of heating, deg/min	Sample wt., mg	Mn(II) compound			Fe(III) compound			Co(II) compound		
		n	E, kcal/mol	log A	n	E, kcal/mol	log A	n	E, kcal/mol	log A
5	25	0.83	47.20	14.83	0.90	51.75	13.37	1.05	56.15	12.43
	50	1.11	44.80	13.17	1.18	48.11	12.10	1.26	52.22	11.37
	75	1.26	40.50	12.36	1.28	46.20	11.83	1.39	50.18	10.40
	100	1.38	38.18	10.73	1.40	44.73	10.17	1.45	48.82	9.90
10	25	1.40	45.10	13.77	1.10	50.60	12.70	1.22	54.17	11.77
	50	1.36	42.40	12.10	1.16	47.33	11.01	1.29	51.77	9.94
	75	1.18	38.69	10.90	1.28	42.46	10.00	1.35	47.31	8.88
	100	1.00	35.27	9.80	1.38	40.12	8.90	1.40	44.22	7.73
15	25	1.09	41.15	12.70	0.95	48.73	11.40	1.16	50.39	10.80
	50	1.17	37.20	11.34	1.19	45.17	10.18	1.27	48.37	9.76
	75	1.30	35.70	9.98	1.28	41.61	9.25	1.13	44.18	8.25
	100	1.00	32.90	8.40	1.43	37.19	8.00	1.37	39.80	7.15

separately for each reaction, for the sample weights and heating rates used (see Table 4). It is obvious that increasing sample weight diminishes the E and log A values, and the same effect is observed with increasing heating rate. This means that the temperature interval corresponding to the thermal decomposition increases with increasing sample weight and heating rate. The explanation of this effect could be simply the limitation of the heat transfer or of the diffusion rate of the gaseous product evolved. This argument is in good agreement with the results given by Zsako [11].

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Zusammenfassung — Ausgehend von den TG-Kurven einiger Komplexe der allgemeinen Formel $[MCl_2(GTD)_2]Cl$ mit GTD = Girard T-Diazetylmonooximkation und M = zentrales Metallion = Mn(II), Fe(III) oder Co(II) wurden die kinetischen Parameter n, A und E (Ordnung der Zersetzungsreaktion, präexponentieller Faktor und Aktivierungsenergie) für die thermischen zersetzungsreaktionen berechnet. Weiterhin wird der Einfluß der experimentellen Bedingungen, wie z. B. Einwaage und Aufheizgeschwindigkeit auf den Wert der berechneten Parameter erläutert.

Резюме — Исходя из ТГ-кривых некоторых комплексов общей формулы $[MCl_2(ЖТД)_2]Cl$, где ЖТД = Жирард Т-диацетилмоноксим катион, а M = двухвалентные марганец, кобальт и трехвалентное железо, вычислены порядок реакции (n), предэкспоненциальный множитель (A) и энергия активации (E) реакции термического разложения. Обсуждено влияние веся образца и скорости нагрева на установленные кинетические параметры.